UDC 666.1.031:666.113.81'28':66.081

THE EFFECT OF BASICITY ON CLARIFICATION OF LEAD SILICATE GLASSES

A. B. Atkarskaya,[1] V. N. Bykov,[1] and M. A. Igumentseva[1]

Translated from Steklo i Keramika, No. 10, pp. 19 – 21, October, 2004.

The effect of the basicity of glass on its bubble content is studied taking silicate optical flints as example. It is found that the increase in bubble content is symbate with the growth in the content of bivalent iron and glass basicity. It is demonstrated that an increase in the concentration of clarifiers does not decrease the bubble content.

One of the main properties of clear glass used in optical elements is a minimal possible quantity of gas-filled inclusions (bubbles) that scatter a light flux. The following main techniques are used for clarifying glass: increasing melting temperature, mechanical stirring and bubbling of the melt with gases, or introduction of clarifying agents into the batch composition. Clarifiers at a high temperature decompose releasing gaseous products that oversaturate the glass melt and result in the formation of bubbles. A bubble growing to a sufficiently large size acquires a substantial float force, rises to the melt surface, and leaves the glass melt. The traditional clarifier for technical glass is sodium sulfate, and for household, special, or optical glass — variable-valence elements oxides (CeO_2, As_2O_3, Sb_2O_3).

The process with the participation of sodium sulfate is based on its decomposition at a temperature above 900°C [1]:

$$Na_2SO_4 \rightarrow Na_2O + SO_2\uparrow + O_2\uparrow.$$

Variable-valence oxides, in particular, As_2O_3 and Sb_2O_3 behave according to a more complex scheme [2]:

$$4RNO_3 \rightarrow 2R_2O + 4NO_2 + O_2, \quad (1)$$

where R = K, Na;

$$As(Sb)_2O_3 + O_2 \rightarrow As(Sb)_2O_3; \quad (2)$$

$$As(Sb)_2O_5 \rightarrow As(Sb)_2O_3 + O_2. \quad (3)$$

Saltpeter in heating decomposes according to reaction (1) and releases oxygen. Reaction (2) takes place in the course of batch loading. The increasing temperature at the clarification stage initiates a reverse process (3) and released oxygen penetrates into the bubbles, whose size grow, and they float purifying the glass melt.

At present the effect of glass composition on the degree of clarification with the participation of sulfates is not sufficiently studied. The probable reason for this is the fact that the compositions of technical and construction glasses exist in the same sodium-calcium-silicate system, which is modified by small additives of other oxides for the purpose of improving its properties. Therefore, the basicity coefficients of such glasses, i.e., the ratios between acid and basic oxides vary within rather narrow intervals. In contrast, the product range of optical and special glasses is diverse, therefore, their basicity coefficients vary significantly. This should have a perceptible effect on glass melt degassing, since with increasing acidity of the melt the variable-valence oxides acting as clarifiers tend to their lower valence state.

Table 1 lists 15 clear optical lead-silicate glasses (flints) specifying their bubble content class, the total content of clarifiers (arsenic and antimony oxides), and the share of bivalent iron calculated by the spectrophotometric method based on the expression from [3].

$$d_{\mathrm{Fe(II)}} = \frac{\chi_\lambda^{\mathrm{Fe(II)}}}{\pi_\lambda^{\mathrm{Fe(II)}}\rho},$$

where $\chi_\lambda^{\mathrm{Fe(II)}}$ is the specific absorption index of iron for wavelength of 900 or 1000 nm, cm^{-1} per 1 wt.% iron; $\pi_\lambda^{\mathrm{Fe(II)}}$ is the volumetric absorption index of bivalent iron calculated for its concentration equal to 1 g per 100 cm^3 of glass; $\pi_\lambda^{\mathrm{Fe(II)}} = 2.26\ cm^2/g$ for $\lambda = 900$ nm and $3.6\ cm^2/g$ for $\lambda = 1000$ nm; ρ is the glass density, g/cm^3.

[1] Institute of Mineralogy, Ural Branch of the Russian Academy of Sciences, Ekaterinburg, Russia.

TABLE 1

Glass	Molar content of clarifiers, %: sum of $As_2O_3 + Sb_2O_3$	Molar content of clarifiers, %: including Sb_2O_3	Estimated values: $d_{Fe(II)}$, %	Estimated values: K_{bas}	Bubble content class, by GOST 3514–78
LF 5	0.22	–	0.8	1.862	A
F 1	0.24	–	1.1	2.296	A
F 2	0.24	–	1.3	2.435	A
F 4	0.24	–	0.8	2.510	A
F 6	0.23	–	1.0	2.317	B
F 8	0.24	–	7.0	4.240	A
F 13	0.32	0.08	0.7	2.421	A
TF 1	0.25	–	2.4	3.355	A
TF 2	0.24	0.11	1.0	3.457	A
TF 3	0.24	0.10	2.1	4.788	B
TF 4	0.69	0.10	2.1	5.646	B
TF 5	0.22	0.10	2.0	3.277	C
TF 7	0.66	0.08	4.5	7.535	C
TF 8	0.11	0.11	3.3	4.157	B
TF 10	0.32	0.13	1.5	8.640	E

The specific absorption index of iron is found from the expression:

$$\chi_{\lambda}^{\mathrm{Fe(II)}} = \frac{-\log T_{\lambda} - D_{\lambda}}{lC},$$

where T_{λ} is the light transmission coefficient of the glass sample for wavelength λ; D_{λ} is the reflection correction for the same wavelength; l is the glass sample thickness, cm; C is the mass content of iron, %.

The coefficient of glass basicity K_{bas} was determined based on the molar content of oxides using the following relationship [4]:

$$K_{bas} = [4.6Al_2O_3 + 4.7(K_2O + Na_2O + BaO + 0.3ZnO + 0.7CaO + 0.7PbO - Al_2O_3)]/\{0.82SiO_2 + [B_2O_3 - (K_2O + Na_2O + BaO + 0.3ZnO + 0.7CaO + 0.7PbO - Al_2O_3)]\}.$$

It is known that, on the one hand, with decreasing K_{bas} the equilibrium Fe(II) ⇔ Fe(III) is shifted to the left and, on the other hand, in accordance with the redox series, an increase in the concentration of As(Sb) oxides shifts this equilibrium to the right:

$$CrO_3 \Leftrightarrow M_2O_3 \Leftrightarrow CeO_2 \Leftrightarrow CuO \Leftrightarrow As_2O_5 \Leftrightarrow Sb_2O_5 \Leftrightarrow Fe_2O_3;$$

$$Cr_2O_3 \Leftrightarrow MnO \Leftrightarrow Ce_2O_3 \Leftrightarrow Cu_2O \Leftrightarrow As_2O_3 \Leftrightarrow Sb_2O_3 \Leftrightarrow FeO. \quad (4)$$

To estimate the combined effect of these two factors, Table 2 shows the correlation of the content of bivalent iron with other parameters for lead silicate glasses.

TABLE 2

Parameter	Average value in interval of variation of molar content, %, of bivalent iron: up to 1.0	1.1 – 2.0	2.1 – 3.0	3.1 – 7.0
$d_{Fe(II)}$, %	0.860	1.475	2.200	4.930
K_{bas}	2.513	4.162	4.596	5.310
Total molar content of clarifiers, %	0.250	0.225	0.390	0.337
Including Sb_2O_3, %	0.038	0.057	0.070	0.063

TABLE 3

Glass	$d_{Fe(II)}$, %	K_{bas}	Molar content of clarifiers, %: sum of $As_2O_3 + Sb_2O_3$	Molar content of clarifiers, %: including Sb_2O_3
LF 5	0.8	1.86	0.22	–
F 6	1.0	2.32	0.23	–
TF 5	2.0	3.28	0.22	0.10
F 13	0.7	2.42	0.32	0.08
TF 10	1.5	8.64	0.32	0.13
F 1	1.1	2.30	0.24	–
F 2	1.3	2.44	0.24	–
F 4	0.8	2.51	0.24	–
F 8	7.0	4.24	0.24	–
TF 2	1.0	3.46	0.24	0.11
TF 3	2.1	4.79	0.24	0.10
TF 4	2.1	5.65	0.69	0.10
TF 7	4.5	7.36	0.66	0.08

Thus, an increase in K_{bas} from 2.51 to 5.31 and the total content of clarifiers from 0.25 to 0.39% leads to an unexpected growth of $d_{Fe(II)}$ from 0.86 to 4.93%. The same is observed in glasses of the $K_2O - B_2O_3 - Al_2O_3 - SiO_2$ system and in multicomponent clear optical crowns containing As_2O_3 (Sb_2O_3) [5, 6]. This dependence can be explained as follows: the reaction between iron and arsenic (antimony) oxides in a glass melt presumably proceeds according to the following reaction:

$$\mathrm{Fe(II) + As[Sb](V) \Leftrightarrow Fe(III) + As[Sb](III)}. \quad (5)$$

With increasing melt basicity the variable-valence elements tend to their higher valence state In the iron — arsenic (antimony) pair the more active element, according to redox series (4), is arsenic (antimony). It acquires the degree of oxidation +5, whereas iron decreases its degree of oxidation to +2, and equilibrium (5) is shifted to the left. Apparently, there is a proportional dependence between the content of bivalent iron and pentavalent antimony (arsenic), which is more evident, the higher the basicity. This is clearly seen from the data in Table 3 which shows the variations in the content of bivalent iron in glasses with different basicity containing equal or close quantities of clarifiers.

It can be seen that with increasing K_{bas} the quantity of bivalent iron in flints with the same or similar contents of

TABLE 4

Parameter	Glass	
	F2	F13
K_{bas}	2.44	2.42
$d_{Fe(II)}$, %	1.3	0.7
Total molar content of clarifiers, %	0.24	0.32

TABLE 5

Bubble content class, by GOST 3514–78	Number of glass grades with the considered bubble class	$d_{Fe(II)}$, %*	K_{bas}*	Total content of clarifiers, %*
A	8	1.6	2.82	0.25
B	4	2.1	4.23	0.32
C	2	2.3	5.41	0.44

* Average value.

clarifiers grows. The deviations registered in the glass series with the total molar content of clarifiers equal to 0.24% may be related to the presence of antimony oxide, which is positioned to the right of arsenic in the redox series (4)

Assuming that the content of Fe(II) grows with an increasing concentration of pentavalent arsenic (antimony), a conclusion can be made in accordance with Eq. (3) that lead silicate glasses with high basicity have poorer clarification and their bubble content is higher than is glasses with more acid compositions. If K_{bas} of different glass compositions are equal or very close, an increase in the concentration of arsenic(antimony) oxide in accordance with series (4) will produce a regular decrease in $d_{Fe(II)}$. This is actually observed in comparing glasses (Table 4).

Table 5 compares data on the bubble content classes of flints (GOST 3514–78) and averaged values characterizing their compositions.

It can be seen that an increase in bubble content is actually symbate with the growth in the content of bivalent iron and increasing basicity of glass. These results can be well explained by Eqs. (2), (3), and (5) describing the process of glass clarification. Reaction (3) responsible for degassing of glass melt is shifted to the left in basic compositions, so that even a consistent increase in the concentration of clarifiers in high-basicity glasses cannot perceptively decrease the content of bivalent iron and decrease the amount of bubbles.

Thus, as the basicity coefficient grows, the content of bivalent iron in flints with an equal or similar content of clarifiers increases.

An increase in the concentration of arsenic (antimony) oxide in lead silicate glasses with equal or similar basicity coefficient decreases $d_{Fe(II)}$.

A growth in the basicity of lead silicate glasses facilitates an increase in the amount of bubbles and is accompanied by an increasing share of bivalent iron.

In high-basicity flints an increase in the concentration of clarifiers does not produce a perceptible decrease in the content of bivalent iron or in the amount of bubbles.

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